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PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-188025

(43)Date of publication of application : 05.07.2002

(51)Int.Cl.

C09D 11/00
B41J 2/01
B41M 5/00
C08G 65/02

(21)Application number : 2001-300185

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(22)Date of filing : 28.09.2001

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(30)Priority

Priority number : 2000308613 Priority date : 10.10.2000 Priority country : JP

(54) ACTINIC ENERGY RAY-CURABLE INK-JET INK

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an actinic energy ray-curable ink-jet ink having low viscosity, excellent in photopolymerizability, having excellent curability in a thick coat, good at heat stability, and to provide the actinic energy ray-curable ink-jet ink good at issue stability with a nozzle, adhesion to printing medium, solvent resistance and water resistance.

SOLUTION: This actinic energy ray-curable ink-jet ink is characterized by being obtained by compounding a liquid component comprising (1) 10-50 wt.% oxirane group-containing compound, (2) 50-90 wt.% oxetane ring-containing compound and (3) 0-40 wt.% vinyl ether compound with (4) a pigment, (5) a photo cationic polymerization initiator and (6) a pigment dispersant.

2003 21 2965

LEGAL STATUS

[Date of request for examination]

09.06.2005

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than
the examiner's decision of rejection or
application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is excellent in photopolymerization nature, and hardenability is good, the stability as ink is good, and the reinforcement of the hardening film is strong and is related with the good activity energy-line hardening mold ink jet ink of the regurgitation stability in a nozzle, the adhesion to recorded media, solvent resistance, and a water resisting property.

[0002]

[Description of the Prior Art] Although there are what distributed thru/or dissolved the oil color in the high boiler, and a thing which dissolved the oil color in the volatile solvent as waterproof good ink jet ink conventionally, since a color is inferior to a pigment in many resistance, such as lightfastness, ink using the pigment as a coloring agent is desired. However, it is difficult to be stabilized and to distribute a pigment to an organic solvent, and it also difficult to secure stable dispersibility and dischargeability. On the other hand in an unabsorbent television object, the solvent in ink does not volatilize, but since the desiccation by evaporation of a solvent is difficult, as for the ink using a high boiler, printing to an unabsorbent base material is impossible.

[0003] In the ink using an volatile organic solvent, good printing can be formed also in an unabsorbent base material by the adhesion of the resin to be used, and volatilization of a solvent. However, since an volatile solvent serves as a principal component of ink, in the nozzle side of a head, desiccation by volatilization of a solvent needs a frequent maintenance very early. Moreover, since remelting nature [essentially as opposed to a solvent in ink] is needed, the resistance over a solvent may not be acquired enough.

[0004] In order to satisfy such a property, the monomers which do not have volatility are used, desiccation with a head is prevented, and use of the ink of the mold stiffened by the thing [giving an activity energy line] on the other hand is also performed. Such ink is opened to JP,62-64874,A, JP,58-32674,A, etc. These ink is used by the continuous type printer, and is mainly the thing of 3 - 5 mPa-s extent as viscosity of ink. Moreover, since this printer carries out the regurgitation of the ink continuously, it can use an volatile solvent together so much, and the viscosity control of ink and volatile grant can also adjust it to preparation comparatively.

[0005] However, it makes the problem of the dissolution swelling of the ink contact ingredient in a printer easy for using an volatile solvent so much to increase the frequency of a maintenance, and to induce in the printer of the method on demand by the piezo-electric element. Moreover, constraint by the dangerous substance as used in [a volatilization solvent] Fire Service Law also becomes large. Then, in the on-demand type printer using a piezo-electric element, it is necessary to consider as ink with little volatile solvent. However, the ingredient used for the ink of an activity energy-line hardening mold was an ingredient with comparatively high viscosity, and it was difficult to design ink with good hardenability and good stability in the viscosity which can carry out the regurgitation by the conventional printer.

[0006]

[Problem(s) to be Solved by the Invention] This invention is hypoviscosity and excellent in photopolymerization nature, and its hardenability in a thick film is very good, and is for thermal stability to offer good activity energy-line hardening mold ink jet ink. Moreover, this invention is to offer the good activity energy-line hardening mold ink jet ink of the regurgitation stability in a nozzle, the adhesion to recorded media, solvent resistance, and a water resisting property.

[0007]

[Means for Solving the Problem] That is, this invention relates to the activity energy-line hardening mold ink jet ink characterized by coming to distribute four pigment for the liquefied component which consists of 10 - 50 % of the weight of 1 oxirane radical content compounds, 50 - 90 % of the weight of 2 oxetane ring content compounds, and 0 - 40 % of the weight of 3 vinyl-ether compounds.

[0008] Moreover, this invention relates to the above-mentioned activity energy-line hardening mold ink jet ink which is non-solvent mold ink further. Moreover, this invention relates to the above-mentioned activity energy-line hardening mold ink jet ink further characterized by including 5 light cationic initiator. Moreover, this invention relates to the above-mentioned activity energy-line hardening mold ink jet ink further characterized by including six pigment agents. Moreover, this invention relates to the above-mentioned activity energy-line hardening mold ink jet ink in which a pigment is characterized by being a detailed pigment with an average grain size of 10-150nm further. Moreover, this invention relates to the above-mentioned ink jet ink characterized by the viscosity in 25 degrees C being 5 - 50 mPa-s. Moreover, this invention relates to the printed matter which comes to print the above-mentioned activity energy-line hardening mold ink jet ink to a base material.

[0009]

[Embodiment of the Invention] Achromatic color inorganic pigments, such as carbon black, titanium oxide, and a calcium carbonate, or the organic pigment of a chromatic color can be used for the pigment contained in the ink jet ink of this invention. As an organic pigment, toluidine red, toluidine MARUN, Hansa Yellow, Insoluble azo pigment, such as benzidine yellow and pyrazolone red, RITORU red, Soluble azo pigment, such as helio bordeaux, pigment scarlet, and Permanent Red 2B, The derivative from vat dye, such as alizarin, an indanthrone, and thioindigo MARUN, Phthalocyanine system organic pigments, such as a copper phthalocyanine blue and Phthalocyanine Green, The Quinacridone system organic pigments, such as the Quinacridone red and the Quinacridone Magenta, Perylene system organic pigments, such as perylene red and perylene Scarlett, Isoindolinone system organic pigments, such as isoindolinone yellow and isoindolinone Orange, Pyran SURON system organic pigments, such as pyran SURON red and pyran SURON Orange, As iso indoline system organic pigments, such as kino FUTARON system organic pigments, such as a thioindigo system organic pigment, a condensation azo system organic pigment, a bends imidazolone system organic pigment, and kino FUTARON yellow, and iso indoline yellow, and other pigments Flavan SURON yellow, acyl amide yellow, nickel azo yellow, copper azomethine yellow, a peri non orange, anthrone Orange, dianthraquinonyl red, dioxazine violet, etc. are mentioned.

[0010] If an organic pigment is illustrated by the Color Index (C. I.) number C. I. pigment yellow 12, 13, 14, 17, 20, 24, 74, 83, and 86 93, 109, 110, 117, 125, 128, 129, 137, 138, 139, 147, 148, 150, 151, 153, 154, 155, 166, 168, 180, 185, C.I. pigment Orange 16, 36, 43, 51, 55, 59, and 61, the C.I. pigment red 9, 48, 49, 52, 53, 57, 97, 122, 123, 149, 168, 177, 180, 192, 202, 206, 215, 216, and 217, 220, 223, 224, 226, 227, 228, 238, 240, the C.I. pigment violet 19, 23, 29, 30, 37, 40, and 50, the C.I. pigment blues 15, 15:1, 15:3, 15:4, 15:6, 22, 60, and 64, C. I. pigment Green 7 and 36, C.I. pigment Brown 23 and 25, and 26 grades are mentioned.

[0011] In the above-mentioned pigment, since lightfastness is excellent, the Quinacridone system organic pigment, a phthalocyanine system organic pigment, a bends imidazolone system organic pigment, an isoindolinone system organic pigment, a condensation azo system organic pigment, a kino FUTARON system organic pigment, an iso indoline system organic pigment, etc. are desirable. As for an organic pigment, it is desirable that it is a detailed pigment with a mean particle diameter of 10-150nm in the measured value by laser dispersion. When the fall of the lightfastness by particle size becoming small when the mean particle diameter of a pigment is less than 10nm arises and it exceeds

150nm, stable maintenance of distribution becomes difficult and it becomes easy to produce precipitation of a pigment.

[0012] Detailed-ization of an organic pigment can be performed by the following approach. That is, mixture which consists of at least three components of the water-soluble mineral salt beyond 3 weight twice of an organic pigment and an organic pigment and a water-soluble solvent is used as clay-like mixture, after scouring strongly and crowding and making it detailed by a kneader etc., it supplies underwater, and it stirs by a high speed mixer etc., and considers as the shape of a slurry. Subsequently, filtration and rinsing of a slurry are repeated and water-soluble mineral salt and a water-soluble, water-soluble solvent are removed. Resin, a pigment agent, etc. may be added to a detailed chemically-modified degree. A sodium chloride, potassium chloride, etc. are mentioned as water-soluble mineral salt. these mineral salt -- more than 3 weight twice of an organic pigment -- it uses in not more than 20 weight twice preferably. If there are few amounts of mineral salt than 3 weight twice, the processing pigment of desired magnitude will not be obtained. Moreover, if [than 20 weight twice] more, the washing processing in a next process will be great, and the substantial throughput of an organic pigment will decrease.

[0013] Especially if it is the solvent which a water-soluble solvent builds the moderate clay condition of an organic pigment and the water-soluble mineral salt used as a crushing assistant, it is used in order to perform sufficient crushing efficiently, and dissolves in water, it will not be limited, but since it will be in the condition that temperature rises and a solvent tends to evaporate at the time of kneading, the solvent of the high-boiling point of 120-250 degrees C of the point of safety to boiling points is desirable. As a water soluble solvent, 2-(methoxy methoxy) ethanol, 2-butoxyethanol, 2-(isopentyloxy) ethanol, 2-(hexyloxy) ethanol, A diethylene glycol, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, the diethylene-glycol monobutyl ether, Triethylene glycol, the triethylene glycol monomethyl ether, A liquid polyethylene glycol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, Dipropylene glycol, dipropylene glycol monomethyl ether, the dipropylene glycol monoethyl ether, a low-molecular-weight polypropylene glycol, etc. are mentioned.

[0014] In order that a pigment may acquire sufficient concentration and sufficient lightfastness in this invention, it is desirable to be contained in 3 - 15% of the weight of the range in ink jet ink.

[0015] oxirane ** the oxirane radical content compound contained in the ink jet ink of this invention is indicated to be by the bottom formula of one or more pieces in a molecule -- [Formula 1]



what is the compound which **** and is usually used as an epoxy resin -- a monomer, oligomer, or a polymer -- all are usable. Well-known aromatic series epoxide, alicycle group epoxide, and aliphatic series epoxide are mentioned concrete conventionally. In addition, epoxide means a monomer or its oligomer below. Two or more sorts of these compounds may be used a kind or if needed.

[0016] A thing desirable as aromatic series epoxide is II or poly glycidyl ether manufactured by the reaction of the polyhydric phenol which has at least one aromatic series nucleus, or its alkylene oxide adduct and epichlorohydrin, for example, II of II of bisphenol A or its alkylene oxide adduct or poly glycidyl ether, hydrogenation bisphenol A, or its alkylene oxide adduct or poly glycidyl ether, a novolak mold epoxy resin, etc. are mentioned. Ethyleneoxide, propylene oxide, etc. are mentioned as alkylene oxide here.

[0017] As alicyclic epoxide, the compound which has cycloalkane rings, such as KISEN or a cyclopentene ring, to at least one cyclo The cyclohexene oxide or the cyclopentene oxide content compound obtained by carrying out epoxidation with suitable oxidizers, such as a hydrogen peroxide and a peroxy acid, is desirable. As an example For example, the Daicel Chemical Industries, Ltd. make, the SEROKI side 2021, SEROKI side 2021A, SEROKI side 2021P, the SEROKI side 2080, the

SEROKI side 3000, the SEROKI side 2000, EPOLEAD GT 301, EPOLEAD GT 302, EPOLEAD GT 401, EPOLEAD GT 403, EHPE-3150, EHPEL3150CE, Made in Union Carbide, UVR-6105, UVR-6110, UVR-6128, UVR-6100, UVR-6216, UVR-6000 grade, etc. can mention.

[0018] JI or poly glycidyl ether of aliphatic series polyhydric alcohol or its alkylene oxide adduct etc. is one of desirable things of aliphatic series epoxide. As the example of representation The diglycidyl ether of alkylene glycol, such as diglycidyl ether of ethylene glycol, diglycidyl ether of propylene glycol, or diglycidyl ether of 1,6-hexanediol, The poly glycidyl ether of polyhydric alcohol, such as JI of a glycerol or its alkylene oxide adduct, or triglycidyl ether, The diglycidyl ether of polyalkylene glycols, such as diglycidyl ether of the diglycidyl ether of a polyethylene glycol or its alkylene oxide adduct, a polypropylene glycol, or its alkylene oxide adduct, etc. is mentioned. Ethyleneoxide, propylene oxide, etc. are mentioned as alkylene oxide here.

[0019] Furthermore, the monoglycidyl ether of the monoglycidyl ether of aliphatic series higher alcohol and a phenol, and cresol etc. can be used other than these compounds. When fast curability is taken into consideration among these epoxide, aromatic series epoxide and alicyclic epoxide are desirable, and especially alicyclic epoxide is desirable.

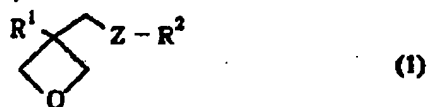
[0020] An oxirane radical content compound is preferably blended 30 to 50% of the weight ten to 50% of the weight among the liquefied component which consists of a vinyl ether compound blended an oxetane ring content compound and if needed. If larger [if there are few oxirane radical content compounds than the above-mentioned numeric value the reinforcement of the hardening film will become weak and the resistance as a printing object will not be acquired, but] than the above-mentioned numeric value, although it becomes good, since viscosity becomes very high and it becomes impossible to apply the resistance of a printing object as ink jet ink, it is not desirable.

[0021] As an oxetane ring content compound in this invention, the compound which has one piece or two oxetane rings or more is mentioned into a molecule.

[0022] As a compound which has one oxetane ring in a molecule, the compound expressed with the following formula (1) can be mentioned.

[0023]

[Formula 2]



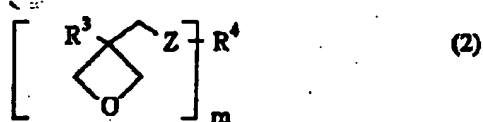
[0024] the inside of a formula (1), and Z -- an oxygen atom or a sulfur atom, and R1 -- a hydrogen atom and a fluorine atom -- The alkyl group of 1-6 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, the fluoro alkyl group of 1-6 carbon numbers, an allyl group, an aryl group, a furil radical or a thienyl group, and R2 The alkyl group of 1-6 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, 1-propenyl radical, 2-propenyl radical, a 2-methyl-1-propenyl radical, The alkenyl radical of 1-6 carbon numbers, such as a 2-methyl-2-propenyl radical, 1-butenyl group, 2-butenyl group, or 3-butenyl group, Aryl groups, such as a phenyl group, benzyl, fluoro benzyl, a methoxybenzyl radical, or a phenoxy ethyl group, The alkyl carbonyl group of 1-6 carbon numbers, such as a propylcarbonyl radical, a butyl carbonyl group, or a pentyl carbonyl group, The alkoxy carbonyl group of 1-6 carbon numbers, such as an ethoxycarbonyl radical, a propoxy carbonyl group, or a butoxycarbonyl radical, the alkoxy carbamoyl group of 1-6 carbon numbers, such as an ethoxy carbamoyl group, a propyl carbamoyl group, or a butyl pentyl carbamoyl group, is expressed.

[0025] As an oxetane ring content compound used by this invention, it sets at an above-mentioned ceremony (1), and is R1. A low-grade alkyl group especially an ethyl group, and R2 As for butyl, a phenyl group or benzyl, and Z, what is an oxygen atom is desirable.

[0026] As a compound which has two or more oxetane rings in a molecule, the compound expressed with the following formula (2) can be mentioned.

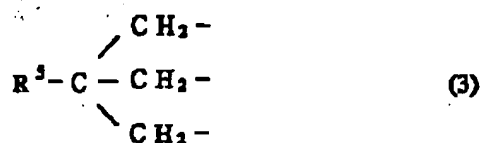
[0027]

[Formula 3]



[0028] the inside of a formula (2), and m -- 2, 3 or 4, and Z -- an oxygen atom or a sulfur atom, and R3 - a hydrogen atom -- The alkyl group of 1-6 carbon numbers, such as a fluorine atom, a methyl group, an ethyl group, a propyl group, or butyl, A phenyl group, the fluoro alkyl group of 1-6 carbon numbers, an allyl group, an aryl group or a furil radical, and R4 For example, the linearity of the carbon numbers 1-12 shown by the bottom formula (3) or a branching alkylene group, linearity or a branching Pori (alkyleneoxy) radical, [0029]

[Formula 4]

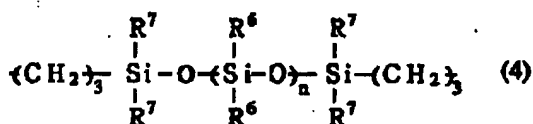


[0030] (R5 expresses low-grade alkyl groups, such as a methyl group, an ethyl group, or a propyl group, among a formula (3).)

[0031] Or the polyad chosen from the group which consists of the following type (4), (5), and (6) is expressed.

[0032]

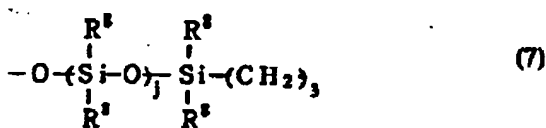
[Formula 5]



[0033] (n expresses the radical chosen from the integer of 0, or 1-2000, and the group to which R6 changes from the alkyl group of 1-10 carbon numbers and the following types (7), such as a methyl group, an ethyl group, a propyl group, or butyl, among a formula (4).)

[0034]

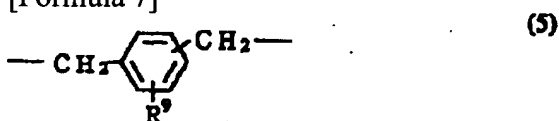
[Formula 6]



[0035] (The alkyl in which j has the integer of 0, or 1-100 among a formula (7), and R8 has 1-10 carbon atoms, and R7 express the alkyl group of the carbon numbers 1-10, such as a methyl group, an ethyl group, a propyl group, or butyl.)

[0036]

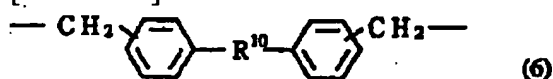
[Formula 7]



[0037] (R9 expresses the alkyl group of 1-10 carbon numbers, such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, or butyl, the alkoxy group of 1-10 carbon numbers, a halogen atom, a nitro group, a cyano group, a sulfhydryl group, a low-grade alkyl carboxylate radical, or a carboxyl group among a formula (5).)

[0038]

[Formula 8]



[0039] R10 expresses an oxygen atom, a sulfur atom, NH, SO and SO₂, CH₂ and C (CH₃)₂, or C(CF₃)₂ among (formula (6).)

[0040] As an oxetane ring content compound used by this invention, it sets at an above-mentioned ceremony (2), and is R3. A low-grade alkyl group especially an ethyl group, and R4 It sets at a ceremony (5) and is R9. It sets at the radical which is a hydrogen atom, a hexamethylene radical, and a ceremony (3), and is R5. An ethyl group and R7 And R8 As for a methyl group and Z, what is an oxygen atom is desirable.

[0041] In a formula (8), r is the integer of 25-200 and R11 is the alkyl group or trialkylsilyl group of carbon numbers 1-4.

[0042] In this invention, two or more kinds may be used together in the compound which has an oxetane ring more than a piece in the above-mentioned molecule as a constituent.

[0043] An oxetane ring content compound is preferably blended 50 to 70% of the weight 50 to 90% of the weight among the liquefied component which consists of a vinyl ether compound blended an oxirane radical content compound and if needed. If there are few oxetane ring content compounds than the above-mentioned numeric value, hardenability will worsen, if larger than the above-mentioned numeric value, hardenability will become good, but since the reinforcement of the hardening film is weak and the resistance as printed matter stops coming out, it is not desirable.

[0044] The vinyl ether compound contained in the ink jet ink of this invention For example, the ethylene glycol divinyl ether, ethylene glycol mono-vinyl ether, The diethylene-glycol divinyl ether, triethylene glycol monovinyl ether, Triethylene glycol divinyl ether, the propylene glycol divinyl ether, Dipropylene glycol divinyl ether, the butanediol divinyl ether, The hexandiol divinyl ether, the cyclohexane dimethanol divinyl ether, Hydroxyethyl mono-vinyl ether, hydroxy nonyl mono-vinyl ether, JI or TORIBI nil ether compounds, such as the trimethylol propane TORIBI nil ether, Ethyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, Octadecyl vinyl ether, cyclohexyl vinyl ether, hydroxy butyl vinyl ether, 2-ethylhexyl vinyl ether, cyclohexane dimethanol mono-vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, and isopropenyl ether-O-propylene carbonate, Mono-vinyl ether compounds, such as dodecyl vinyl ether, diethylene-glycol mono-vinyl ether, and octadecyl vinyl ether, etc. are mentioned.

[0045] When hardenability, adhesion, and surface hardness are taken into consideration among these vinyl ether compounds, JI or a TORIBI nil ether compound is desirable, and especially a divinyl ether compound is desirable. In this invention, although one sort of the above-mentioned vinyl ether compound may be used independently, you may use it, combining two or more sorts suitably.

[0046] A vinyl ether compound is the combination component of arbitration, and hypoviscosity-ization required of ink jet ink can be realized by making it blend. Moreover, improvement in a cure rate can also be performed. 0 - 20 % of the weight is preferably blended zero to 40% of the weight among the liquefied component which a vinyl ether compound becomes from an oxirane radical content compound and an oxetane ring content compound.

[0047] As an optical cationic initiator used by this invention An aryl sulfonium salt derivative For example, (Union Carbide 6990 [SAIRA cure UVI-], SAIRA cure UVI-6974, ADEKAOPUTOMA SP-150 by Asahi Denka Kogyo K.K., ADEKAOPUTOMA SP-152, ADEKAOPUTOMA SP-170, ADEKAOPUTOMA SP-172), Acid generators, such as an allyl compound iodonium salt derivative (for example, RP-2074 made from low DIA), an allene-ion complex derivative (for example, Ciba-Geigy IRUGA cure 261), a diazonium salt derivative, a triazine system initiator, and other halogenides, are mentioned. As for a cationic initiator, it is desirable to make it contain by the ratio of 0.2 - 20 weight section to the compound 100 weight section which has an alicyclic epoxy group. It is difficult for the content of a polymerization initiator to obtain a hardened material under in the 0.2 weight section, and

even if it makes it contain exceeding 20 weight sections, the further improvement effectiveness in hardenability cannot be found. These light cationic initiator can choose and use one sort or two sorts or more.

[0048] As a photopolymerization accelerator, an anthracene and an anthracene derivative (for example, ADEKAOPUTOMA SP-100 by Asahi Denka Kogyo K.K.) are mentioned. These photopolymerization accelerators can be used combining one sort or plurality.

[0049] As a pigment agent of this invention, the salt of hydroxyl-group content carboxylate, and long-chain poly amino AMAIDO and high molecular weight acid ester, The salt of the amount polycarboxylic acid of giant molecules, the salt of long-chain poly amino AMAIDO and polar acid ester, The amount partial saturation acid ester of macromolecules, a macromolecule copolymerization object, denaturation polyurethane, denaturation polyacrylate, A polyether ester mold anionic surface active agent, a naphthalene sulfonic-acid formalin condensate salt, An aromatic series sulfonic-acid formalin condensate salt, polyoxyethylene alkyl phosphoric ester, the polyoxyethylene nonylphenyl ether, stearyl amine acetate, a pigment derivative, etc. can be mentioned.

[0050] As an example of a pigment agent, it is BYK. The product made from Chemie "Anti-Terra-U (poly amino AMAIDO phosphate)", "Anti-Terra-203 / 204 (the amount polycarboxylic acid salt of giant molecules)", "Disperbyk-101 (poly amino AMAIDO phosphate and acid ester), 107 (hydroxyl-group content carboxylate) 110 (copolymerization object containing an acid radical), 130 (poly AMAIDO), 161, 162, 163, 164, 165, 166, 170" (macromolecule copolymerization object), "400", "Bykumen" (the amount partial saturation acid ester of macromolecules), "BYK-P104, P105" (the amount partial saturation acid polycarboxylic acid of macromolecules), "P104S, 240S (the amount partial saturation acid polycarboxylic acid of giant molecules and silicon system)" and "Lactimon (a long-chain amine, partial saturation acid polycarboxylic acid, and silicon)" are mentioned.

[0051] Moreover, Efka The product made from CHEMICALS "Efka 44, 46, 47, 48, 49, 54, 63, 64, 65, 66, and 71,701,764,766", "Efca polymer 100 (denaturation polyacrylate) and 150 (aliphatic series system denaturation polymer), 400, 401, 402, 403, 450, 451, 452, 453 (denaturation polyacrylate), 745 (copper-phthalocyanine system)" and the Kyoisha chemistry company make "FUOREN TG-710 (urethane oligomer), "Flow non SH-290, SP-1000", poly flow No.50E, No.300 (acrylic copolymerization object)" and made in Kusumoto Chemicals "Despa Ron KS-860, 873SN, 874 (giant-molecule dispersant), #2150 (aliphatic series multiple-valued carboxylic acid), and #7004 (polyether ester mold)" are mentioned.

[0052] Furthermore, the Kao Corp. make DEMORU RN and N (naphthalene sulfonic-acid formalin condensate sodium salt), MS, C, SN-B (aromatic series sulfonic-acid formalin condensate sodium salt), "EP" and "HOMOG E Norian L-18 (polycarboxylic acid mold macromolecule), emulgen 920, 930, 931, 935, 950, and 985 (polyoxyethylene nonylphenyl ether), "ASETAMIN 24 (coconut amine acetate) and 86 (stearyl amine acetate)", "The Zeneka Co. make The Sol Spurs 5000 (phthalocyanine ammonium salt system), 13240, 13940 (polyester amine system), 17000 (fatty-acid amine system), 24000, 32000", and daylight chemical company make "NIKKORU T106 (polyoxyethylene sorbitan mono-olate), MYS-IEX (polyoxyethylene monostearate), Hexagline 4-0 (hexa glyceryl tetra-olate)" etc. is mentioned.

[0053] As for the pigment agent of this invention, it is desirable to make a dispersant contain in 0.1 - 10% of the weight of the range in ink.

[0054] The ink jet ink of this invention is manufactured by using the usual dispersers, such as a sand mill, and distributing a pigment with an activity energy-line hardenability compound and a pigment agent. It is desirable to create the concentration liquid of pigment high concentration beforehand, and to dilute with an activity energy-line hardenability compound. Also in distribution by the usual disperser, sufficient distribution is possible, since for this reason superfluous distributed energy does not start and great distributed time amount is not needed, it is hard to cause the deterioration at the time of distribution of an ink component, and ink excellent in stability is prepared. As for ink, it is [3 micrometers or less of apertures] still more desirable to filter with a filter 1micro or less.

[0055] As for the ink jet ink of this invention, it is desirable that the viscosity in 25 degrees C adjusts 5 - 50 mPa-s and more highly. The regurgitation property stabilized also in the head with a high frequency

of 10-50kHz is shown from the head which has the frequency of 4-10kHz especially usual [viscosity / in 25 degrees C] in the ink of 5 - 50 mPa-s. When viscosity is less than 5 mPa-s, the fall of the imitation nature of the regurgitation is accepted in the head of high frequency, and when exceeding 50 mPa-s, though the fall device of the viscosity by heating is included in a head, the fall of the regurgitation itself is produced, the stability of the regurgitation becomes poor, and it stops being able to carry out the regurgitation at all.

[0056] Moreover, as for the ink jet ink of this invention, in a piezo head, it is desirable to consider as the electric conductivity below 10microS/cm, and to consider as ink without the electric corrosion inside a head. Moreover, in a continuous type, the electric conductivity by the electrolyte needs to be adjusted and it is necessary to adjust to the electric conductivity of 0.5 or more mS/cm in this case.

[0057] All the extensive synthetic resin currently used for the application of the conventional various kinds as a synthetic-resin base material used by this invention is applicable, polyester, a polyvinyl chloride, polyethylene, polyurethane, polypropylene, acrylic resin, a polycarbonate, polystyrene, acrylonitrile-butadiene-styrene copolymer, polyethylene terephthalate, polybutadiene terephthalate, etc. are mentioned, and, specifically, the thickness or the configuration of these synthetic-resin base materials are not limited at all.

[0058] In order to use the ink jet ink of this invention, this ink jet ink is first supplied to the printer head of the printer for ink jet recording methods, and activity energy lines, such as ultraviolet rays or an electron ray, are irradiated discharge and after that on a base material from this printer head. This hardens the constituent on print media promptly.

[0059] In addition, as the light source of an activity energy line, when irradiating ultraviolet rays, for example, a mercury arc lamp, a xenon arc lamp, a fluorescence lamp, a carbon arc lamp, a tungsten-halogen copy lamp, and sunlight can be used. Although it is made to usually harden with the electron ray of the following 300eV energy when making it harden with an electron ray, it is possible to also make it harden with the exposure of 1 - 5Mrad in an instant.

[0060]

[Example] Hereafter, it explains based on an example. The section in an example and % show weight section and weight %, respectively.

It distributed for 4 hours by having put both the pigment shown in one to example 8 table 1, the dispersant [and], the oxirane radical content compound, the oxetane ring content compound, and the vinyl ether compound into the sand mill, and the activity energy-line hardening mold ink undiluted solution was obtained. Subsequently, after making it mix quietly, the pressure filtration of this was carried out with the membrane filter, and activity energy-line hardening mold IJ ink was obtained, until it added the photoinitiator to the ink undiluted solution and the photoinitiator dissolved. This ink printed by IJ printer which has a piezo head to various base materials (a polycarbonate, polystyrene, ABS (acetonitrile-styrene-butadiene copolymer), a polyvinyl chloride, polyethylene terephthalate, polybutylene tele phthalate), and hardened the condition for 10m/of bearer rates of a printing hand-ed after that with UV irradiation equipment (metal-halide-lamp 1 LGT: output 120W).

[0061]

[Table 1]

		1	2	3	4	5	6	7	8
顔料	P1	5	5						
	P2			5	5				
	P3					5	5		
	P4							5	5
オキシラン基含有化合物	モリナド 3000	50	20	5	10	20	10	40	40
	UVR6110		10	10		10	20		5
オキセタン基含有化合物	XDO			50					80
	POX	90	70				90		
	OXA				50	60		70	
ビニルエーテル化合物	DVE-3	10	40	40	10		40	10	20
顔料分散剤	32000	3	3	3	3	3	3	3	3
開始剤	SP-150	10					10		
	SP-170				10	10			10
	UVI6990		10	10				10	

数字は部数を示す。

[0062] The compound of front Naka shows the following. A figure shows number of copies.

A pigment, P1 Crude copper phthalocyanine (a "copper phthalocyanine" by TOYO INK MFG. CO., LTD.): The 250 sections, the sodium chloride:2500 section, and the polyethylene-glycol (Tokyo formation the "polyethylene glycol 300" by shrine):160 section were taught to the 1-gallon kneader made from styrene (the Inoue factory company make), and were kneaded for 3 hours. Next, this mixture was fed into 2.5l. warm water, after stirring by the high speed mixer for about 1 hour and considering as the shape of a slurry, heating at about 80 degrees C, filtration and rinsing were repeated 5 times and the processing pigment which subsequently spray-dried and was dried was obtained except for the sodium chloride and the solvent.

- P2 Quinacridone system red pigment (product made from Ciba Geigy "SHINKASHIA Magenta RT-355-D"): The 250 sections, the sodium chloride:2500 section, and the "polyethylene-glycol 300":160 section were taught to the 1-gallon kneader made from styrene, and the processing pigment was obtained like P1.

- P3 Bends imidazolone system yellow pigment (Hoechst [A.G.] make "HOSUTA palm yellow H3G"): The 250 sections, the sodium chloride:2500 section, and the "polyethylene-glycol 300":160 section were taught to the 1-gallon kneader made from styrene, and the processing pigment was obtained like P1.

- P4 Carbon black pigment "Printex 150T" (Degussa AG make)

[0063] An oxirane radical content compound and SEROKI side 3000 Alicyclic epoxy (die cel company make)

- UVR6110 Alicyclic epoxy (made in Union Carbide)

An oxetane ring content compound, XDO 1 and 4-screw [(3-ethyl-3-OKISETANIRU) methoxy] methyl} benzene (Toagosei make), POX 3-ethyl-3-(phenoxyethyl) oxetane (Toagosei make), OXA 3-ethyl -3 - ***** is carried out and it is a methyl oxetane (Toagosei make) vinyl ether compound and DVE-3. Triethylene glycol divinyl ether (ISP company make) [0064] A dispersant, 32000 Aliphatic series denaturation system dispersant (the "Sol Spurs 32000" Zeneka Co. make)

[0065] An initiator and SP-150 Triphenylsulfonium salt ("ADEKAOPUTOMA SP-150" Asahi electrification company make) -SP-170 Triphenylsulfonium salt ("ADEKAOPUTOMA SP-170" Asahi electrification company make) -UVI6990 triphenylsulfonium salt (made in "SAIRA cure UVI6990" Union Carbide) [0066] It distributed for 4 hours by having put both the pigment shown in one to example of comparison 4 table 2, the dispersant, and the monomer into the sand mill, and the activity energy-line hardening mold IJ ink undiluted solution was obtained. Subsequently, after making it mix quietly, the pressure filtration of this was carried out with the membrane filter, and activity energy-line hardening mold IJ ink was obtained, until it added the photoinitiator to the ink undiluted solution and the photoinitiator dissolved. This ink printed to the above-mentioned base material by IJ printer which has a piezo head, and hardened the condition for 10m/of bearer rates of a printing hand-ed after that with UV

irradiation equipment (metal-halide-lamp 1 LGT: output 120W).

[0067]

[Table 2]

		1	3	4	5
顔料	P1	5			
	P2		5		
	P3			5	
	P4				5
オキシラン基含有化合物	トナール 3000		80	80	5
	UVR6110	50			
オキセタン基含有化合物	XDO	10			
	POX	10	20	50	
	OXA	10			50
ビニルエーテル化合物	DVE-3	50	30	30	30
顔料分散剤	32000	3	3	3	3
開始剤	SP-150	10			
	SP-170			10	10
	UVI6990		10		

数字は部数を示す。

[0068] The same thing as what was used for examples 1-8 was used for the compound of front Naka. A figure shows number of copies.

[0069] The following evaluation was performed about the ink and the printed matter which were obtained in examples 1-8 and the examples 1-4 of a comparison. A result is shown in Table 3.

[0070]

[Table 3]

番号	粘度	硬化性	経時安定性	膜強度
実施例 1	34.5	1	○	○
2	30.2	1	○	○
3	18.6	1	○	○
4	18.2	1	○	○
5	38.6	1	○	○
6	22.5	1	○	○
7	33.2	1	○	○
8	32.8	1	○	○
比較例 1	46.7	8	○	×
2	34.1	3	△	×
3	21.3	1	△	×
4	30.2	未硬化	○	×

[0071] The value when measuring the viscosity of the evaluation approach [viscosity] ink of front Naka at 25 degrees C using a Brookfield viscometer. A unit is the count of pass of a KOKOMBEA UV lamp until a tuck is lost by mPa-s [hardenability] finger touch.

25 degrees C estimated the distributed condition after one-month preservation for [with the passage of time stability] ink by viewing and viscosity change.

○ : -- with [generating of precipitate is not accepted and] no change of viscosity -- generating of **;precipitate is not accepted but viscosity is accepted for generating of increment x;precipitate.

[Film reinforcement] The pawl scratched the reinforcement of the hardening film and it carried out by the trial.

○ : -- **: which cannot be taken at all even if it scratches -- [Effect of the Invention] which can be taken

a little if it scratches strongly and which can be easily taken if it x: scratches In the ink jet which distributed the pigment to the activity energy-line hardenability compound, by hypoviscosity, the reinforcement of the hardening film was strong, hardenability was good, and stability could be good and was able to obtain ink jet ink with the sufficient regurgitation stability in a nozzle by this invention. Moreover, the record object recorded in the ink jet ink of this invention has high transparency, is excellent in the resistance of a record object, and excellent in gloss.

[Translation done.]